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CAESIUM, RUBIDIUM, AND LITHIUM

BY

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By R. M. Santmyers[2]

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INTRODUCTION

Caesium, rubidium, and lithium are sometimes described as the minor or rarer alkali metals. They generally occur together in nature, although lithium is distributed more widely and is far more abundant than either of the other two. The chemical, and even the physical, properties of these three elements can best be considered in conjunction with the more familiar members of the alkali group, sodium and potassium.

The five elements lithium, sodium, potassium, rubidium, and caesium show an interesting gradation in properties from member to member with the increase in atomic weights. All are silvery white and soft enough to be cut with a knife. They tarnish rapidly in air and decompose water at ordinary temperatures. The lowest temperature at which the action of the several metals on water can be detected is -98°C. for sodium, -105°C. for potassium, -108°C. for rubidium, and -116°C. for caesium. The chemical activity appears to increase steadily from lithium to caesium. All manifest a remarkable affinity for oxygen, and caesium and rubidium ignite spontaneously if placed in dry oxygen at room temperature. On the other hand, sodium and lithium have feebler affinities. All the metals, however, lose their luster at once when exposed to air. Sodium, potassium and lithium are stored in an oxygen-free liquid, such as water-free ether, naptha, or kerosene, but rubidium and caesium must be kept in a vacuum.

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[1] The Bureau of Mines will welcome reprinting of this article, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6215."

[2] Mineral specialist, rare metals and nonmetals division, U. S. Bureau of Mines.

Physical properties of the alkali metals[1]

	Lithium	Sodium	Potassium	Rubidium	Caesium
Atomic weight	6.94	23.00	39.10	85.45	132.81
Specific gravity	.534	.9723	.859	1.525	1.903
Atomic volume	13.1	23.7	45.4	55.8	71.0
Melting point, Centigrade	180°	97.6°	65.5°	39°	28.5°
Do. Fahrenheit	356°	208°	117.9°	102.2°	78.3°
Boiling point, Centigrade	+1400°	877.5°	757°	696°	670°
Do. Fahrenheit	2552°	1611°	1394°	1284°	1238°
Specific heat at 0° C. ..	0.941	.2811	.1728	.0802	.0522
Coefficient of expansion.	- - -	.000274	.000282	.000338	.000345
Heat of fusion (cal.) ...	- - -	27.21	14.67	6.144	3.766

[1] Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. 2, London, 1922, p. 880.

Different values have been reported for the specific gravities, presumably because it is difficult to prepare the absolutely pure metals. All, however, are exceptionally light and have large atomic volumes. Lithium, in fact, is only a little more than half as heavy as water and is the lightest element solid at ordinary temperatures. It is the only one of the five that fails to melt below the boiling point of water, and its melting point is only 180°C.

The oxides and hydroxides of the alkali metals are markedly basic. The physical properties of the salts - solubility in water, molecular volume, optical properties, and variation in form of the crystals - show the same order of variation as the atomic weights of the elements. The salts of the metals - nitrates, chlorides, sulphides, sulphates, phosphates, carbonates, etc., are nearly all soluble in water. However, the salts of lithium, notably the carbonated phosphate and fluoride, are much less soluble than the corresponding salts of the other members; in this respect lithium seems to be a sort of connecting link between the members of the alkali group and the alkaline earth group, of which calcium is the first member. The alkali sulphates form characteristic isomorphous alums, but lithium alum appears to be so soluble that it has not yet been crystallized. Sodium resembles lithium in the solubility of its chloroplatinate, acid tartrate, and alum, and this resemblance is so strong that the five alkali metals are sometimes divided into two classes according to whether the chloroplatinates (1) are readily soluble (sodium and lithium), or (2) are comparatively insoluble (potassium, rubidium, and caesium).[3]

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[3] Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 2, London, 1922, pp. 442-443 and 880.

HISTORY

Had it not been for the spectroscope the discovery of the elements caesium and rubidium would doubtless have been long postponed. In 1846 C. F. Plattner analyzed the mineral pollucite from the island of Elba and was mystified by the fact that the constituents apparently totaled only 92.75 per cent. Careful search failed to reveal any error in analysis or any constituents that had been overlooked, and the problem remained unsolved until 1860, when caesium was discovered. In 1864, four years after the discovery of caesium, Pisani repeated the analysis of pollucite and found that the alkali metal Plattner had called potassium was in reality caesium. When corrections were made for the differences in atomic weights of caesium and potassium Plattner's results were found to be quite accurate.

In 1860 Bunsen used the newly devised spectroscope to examine the mineral constituents of the spring water at Durkheim, and discovered two blue lines of unknown origin. He bacame convinced that they were characteristic of a new alkali metal and proposed the name caesium from the Greek for "sky blue." Forty tons of water were evaporated in order to get enough caesium salts for experiments.

Caesium was the first element discovered by the use of the spectroscope, and a year later (in 1861) rubidium was discovered by the same means. Bunsen and Kirchhoff were then studying the alkaline constituents extracted from samples of lepidolite from Saxony and found that the chloroplatinate precipitate contained a salt somewhat less soluble than the potassium salt and whose spectrum had new lines in the violet, blue, green, yellow, and red. Especially prominent were two red lines lying beyond Fraunhofer's line in the outermost portion of the red solar spectrum, hence the name rubidium, "dark red," was suggested for this new element. Such small amounts were present in the mineral with which Bunsen and Kirchhoff were working that they used 150 kilograms to obtain enough of the new element to permit a study of its properties.

Lithium had been isolated some years before caesium and rubidium were found and was discovered by Aug. Arfvedson. While working in Berzelius' laboratory in 1817 he found a new element in the minerals petalite and spodumene and named it lithium, meaning "stony," in contrast to sodium and potassium, which are widely distributed in plants and animals. This element differed from the known alkali metals in the insolubility of its carbonate, the hygroscopic nature of its chloride, and the low melting points of the chloride and sulphate.

Later work of Bunsen and Kirchhoff with the spectroscope showed that lithium was also distributed very generally in animal and plant tissues, although usually in extremely small quantities.

MINERALS AND ORES

Although the minerals from which caesium, rubidium, and lithium may be extracted are distributed rather widely in nature, the known minerals and deposits rich enough to furnish large supplies are few. Most of the minerals contain at least a trace of all three elements. Several minerals comparatively rich in lithium are known, but only one (pollucite) is high in caesium, and no definite rubidium minerals are known. Lepidolite, the best known of the lithium minerals in a number of localities carries from a trace to more than 3 per cent of rubidium oxide (Rb_2O), and a small fraction of a per cent of caesium oxide (Cs_2O). Lepidolite, in fact, carries more rubidium than any other known mineral, although on very incomplete data a tiny specimen of a rubidium mineral, rhodozite, from the Urals has been described. The principal lithium minerals are lepidolite, amblygonite, and spodumene.[4]

Lepidolite, the richest rubidium-bearing mineral, is a complex lithia-mica containing 4 to 6 per cent of Li_2O, as much as 0.77 per cent of Cs_2O, and as much as 3 per cent of Rb_2O. Although the clean mineral may contain 6 per cent of Li_2O, it usually contains nearer 4 per cent, and, as mined, the mica is very impure and the lithia content is usually nearer 2 per cent, so that it is not as important as a source of lithia salts as amblygonite or spodumene.

Amblygonite, a lithium aluminum fluophosphate ($2LiF.Al_2O_3.P_2O_5$), carries 8 to 9 per cent of Li_2O and is one of the principal sources of lithium. It does not contain appreciable quantities of caesium or rubidium.

Spodumene, a lithium-aluminum silicate ($Li_2O.Al_2O_3.4SiO_2$), carries 4 to 8 per cent of Li_2O.

Sundry other minerals, notably petalite ($L_2O.Al_2O_3.4SiO_2$) and triphylite ($LiFePO_4$ with some manganese) and the grades to lithiophilite ($LiMnPO_4$ with some iron) contain considerable percentages of lithium and may contain very small quantities of rubidium and caesium, but the total amounts available are too small for them to be of importance as a source of lithium. All the minerals named are found in pegmatites. Lithium has been found in more than 40 other minerals in quantities ranging from spectroscopic traces to more than 9 per cent (the last in a mica), but none of the minerals are important as a possible source of lithium under present known conditions.

The following table gives typical analyses of lithium minerals mined as sources of lithium compounds.

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[4] For further discussion of this mineral see: Myers, W. M., Mica-- Part I. I. C. 6205, Bureau of Mines.

Typical composition of lithium minerals mined as sources of lithium compounds[1]

	Spodumene	Lepidolite	Amblygonite
Silica (SiO_2)	64	51	- -
Alumina (Al_2O_3)	27	27	34
Lithia (Li_2O)	7	4	9
Potash (K_2O)	- -	11	- -
Phosphoric acid (P_2O_5)	- -	- -	48
Water (H_2O) combined	- -	2	5
Fluorine (F)	- -	7	5
Iron, manganese, lime, magnesia, soda	2	1	1
	100	103	102
Less oxygen equivalent of fluorine	- -	3	2
	100	100	100

[1] Schaller, W. T., Lithium Minerals. Mineral Resources of the United States, 1916; Part II, Nonmetals. U. S. Geol. Survey, 1919, pp. 8-12.

TESTS FOR IDENTIFICATION[5]

Caesium and rubidium, being similar to potassium, may be precipitated as platinic chlorides ($CsPtCl_6$ or $RbPtCl_6$). These precipitates, which are much more insoluble than the corresponding potassium compound, precipitate in a more finely divided condition, and the caesium salt has a paler color. For positive identification it is best to heat some of the precipitate on a platinum wire and examine the flame with a spectroscope.

The crimson color that lithium imparts to a flame usually serves for its identification. The color of a pure lithium flame is nearly monochromatic, showing when examined with the spectroscope one bright crimson and one very faint yellowish-red band. Sodium has a disturbing influence, but this is mitigated by the fact that lithium is more volatile than sodium. When, therefore, the assay is first introduced into the flame the red of lithium will show before the yellow of sodium; and when the flame is strongest, if the position of the assay is changed to where the heat is less intense, the yellow will disappear first and the red of lithium will be seen distinctly. When the proportion of sodium is large, however, the spectroscope must be employed.

USES

Caesium and rubidium appear on the market as salts, mainly chlorides, nitrates, and hydroxides, and only rarely in their metallic state.

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[5] Brush, Geo. J., and Penfield, S. L., Manual of Determination Mineralogy. New York, 1901. Cesium, p. 58; rubidium, p. 107; and lithium, p. 90.

There has been little demand for caesium. The principal use at present is in the manufacture of radio tubes. The caesium is introduced into the tubes in the form of chloride, mixed with magnesium or calcium, and is compressed into small tablets or "pills"; at one stage in the manufacture of the tube the pill is flashed, eliminating the last trace of air and thus securing the desired vacuum. The caesium chloride supplies positive ions at the surface of the filament.

Both caesium and rubidium are employed to a limited extent in the manufacture of photo-electric cells. Rubidium, however, appears to be more suitable for this than caesium, because an extremely thin layer can be applied on the inner side of the glass. In the manufacture of these cells the metal, either caesium or rubidium, is introduced in excess but later is removed entirely except for the molecular layer that has formed on the silver or other base-metal electrode. The photo-emission of the molecular layer of metal is greater than that of the massive metal.

Rubidium compounds are employed in larger amounts than the metal because they have proved their importance as reagents in microchemistry; their ability to form crystalline compounds readily, makes them of great value in this important and rapidly developing field.

Unlike caesium and rubidium, lithium minerals are used both as they occur in nature and as sources of lithium salts and compounds. One of the earliest uses for lithium salts was in the manufacture of lithia water and other medicinal preparations, but the use of lithia water has declined rapidly in recent years. The carbonate, phosphate, nitrate, and organic compounds are used for medicinal purposes.

At present the largest use for lepidolite is in the manufacture of opal glass. It is ground and added, either fused or unfused, to the glass batch. Lepidolite to be used in glass-making must be free from tourmaline and other possible coloring materials. Patents cover the use of the mineral for this purpose.

In pyrotechnics, lithium chloride is used to impart a crimson color to fireworks and signal lights. Fairly large quantities of several of the compounds of lithium are used in other ways. For example, lithium hydroxide is used in alkaline electrolyte storage batteries, lithium bromide and iodide are employed in photography, and lithium carbide is used in Roentgen-ray experiments.

Lithium metal, as such, has no known use owing to its softness and rapid deterioration by water, but in recent years considerable research has been made to determine the possibilities of alloying lithium with other light metals such as beryllium and aluminum. In 1920 United States patent 1,333,965 was issued to Frank A. Fahrenwald for an alloy of extreme lightness, fair permanence and considerable hardness, in which the component parts were lithium and beryllium.

The beryllium protects the lithium from oxidation by moisture or heating and from further action if oxidation has begun by producing upon the surface of the alloy a closely adherent, finely textured insoluble oxide that prevents further oxidation. The lithium content may be as high as 25 per cent. This alloy apparently does not corrode faster than iron, and its specific gravity is only about 1.5. By increasing the proportion of lithium to about 65 per cent an alloy as light as water can be produced, and although such an alloy corrodes fairly rapidly in the presence of water it can be protected sufficiently for many purposes by plating or covering. If the percentage of lithium is increased slightly above 65 per cent, small quantities of aluminum or zinc may be added to increase the hardness and strength, but the alloy will retain a specific gravity little or no greater than that of water.

Aluminum to which a very small percentage of lithium has been added has been used to a limited extent in Germany for trucks and bed frames of street and railway cars. This alloy is exceptionally strong.

Since lithium oxide has a low fusion point, lithium has been suggested as a deoxidizer of copper.

SOURCES OF SUPPLY AND PRODUCTION

California

The minerals from which caesium, rubidium, and lithium may be extracted occur in only a few regions in the United States, principally in California, South Dakota, New Mexico, and Maine.

The Stewart mine, in a pegmatite about 1½ miles northeast of Pala, San Diego County, Calif., has produced lepidolite at intervals for a number of years. Amblygonite and spodumene are also found in the deposit, but in small quantity. The caesia (Co_2O) content of the lepidolite is about 0.3 per cent, whereas the lithia (Li_2O) content ranges from 2 to 6 per cent. Mining operations on this property are very simple. Tunnels are run through the country rock to the lepidolite, which is blasted out, rolled down the hill, and shipped without further treatment. Little foreign or waste material has to be removed. Practically all of the shipments have been made to glass companies in the east.

South Dakota

The Etta mine, in a large oval mass of very coarse pegmatite near Keystone, is the best known producer of lithium-bearing minerals in South Dakota, but was originally opened for mica. Spodumene in huge crystals, carrying 4 to 6 per cent of Li_2O, is the only lithium mineral. The alteration of the spodumene at this mine is a feature of considerable scientific interest and much economic importance. Various degrees of alteration are shown from fresh spodumene with a hardness of 6.5 to 7 and a specific gravity of approximately 3.2 to much altered material with a hardness of only 2.5 and a specific gravity of approximately 2.6.

The unaltered spodumene is white and more or less translucent, but part is altered to ash-gray and to various tints of dull green, or less commonly to red or black. The alteration is accompanied by a loss in lithia content and a gain in potash. The alteration may have been brought about by the same hot waters which originally formed the spodumene but which with changing conditions attacked it, dissolved out the lithia, and replaced it with potash.

The Maywood Chemical Co., Maywood, N. J., owners and operators of the Etta Mine, also own the Tin Mountain mine, 6 miles west of Custer, and from it are producing large quantities of spodumene and amblygonite as well as some beryl and pollucite. This property is the largest producer of pollucite in the United States. The Tin Mountain mine is also one of the largest producers of lithium minerals, ranking second to the Etta Mine. Amblygonite occurs at several other mines in this region; the Beecher claim, 5 miles northeast of Pringle, owned by Green & Collingwood, is one of the more important sources of amblygonite, and The Peerless and Hugo mines, close to the Etta mine, and the Bob Ingersoll, 2½ miles northwest of Keystone, also produce large quantities. A total production of several thousand tons of amblygonite has been reported from the mines in this area.

Triphylite in masses, some of which weigh hundreds of pounds, has been found in the Lost Bonanza, Dyke, Hugo, and other pegmatites.

Lepidolite is important only in the Bob Ingersoll pegmatite.

The following table taken from reports of South Dakota authorities shows the value of the lithia minerals produced in the Black Hills, South Dakota. It includes only spodumene and amblygonite. Practically the entire production is shipped to the Eastern States and used in the manufacture of lithium salts and compounds.

Production of lithia minerals in the Black Hills, South Dakota[1]

Year	Value
1898-1913	[2] $143,000
1914	1,150
1915	5,120
1916	10,740
1917	25,620
1918	82,500
Jan. 1, 1919 - June 30, 1920	69,390
July 1, 1920 - June 30, 1921	43,250
July 1, 1921 - June 30, 1922	9,040
July 1, 1922 - Dec. 31, 1922	15,750
1923	39,125
1924	53,833
1925	40,900
1926	32,000
1927	13,140
1928	21,450
Total	$606,008

NOTE: Figures for 1914-1926, inc., are from the annual reports of the State mine inspector, Otto Ellerman.

1/ Connolly, Joseph P., and O'Harra, Cleophas C., The Mineral Wealth of the Black Hills. South Dakota School of Mines, Bulletin 16, May, 1929, p. 247.

2/ Ziegler, Victor, Mineral Resources of the Harney Peak Pegmatites. Min. and Sci. Press, vol. 108, 1914, pp. 604-608, 654-656.

New Mexico

Lepidolite has been produced from one pegmatite in New Mexico for the past five or six years. The deposit is 9 miles east of Dixon, Rio Arriba County, and 12 miles from Embudo, the nearest railroad station. The output is shipped to the East and used in the manufacture of opalescent glass. As shipped it carries 3.25 per cent of Li_2O. Some lepidolite from this deposit carries many tiny crystals of microlite (calcium tantalate), which must be picked from the ore as it has a detrimental effect in glass-making.

Other States

Small quantities of lepidolite have been shipped from Mount Mica near Paris, and from pegmatites 7 miles south of Andover, Maine. In recent years a few thousand pounds of pollucite have been produced from three pegmatites west of Buckfield, and larger quantities have been shipped from the pegmatites in the town of Newry, 7 miles shouth of Andover. All the localities are in Oxford County.

Lepidolite occurs in some quantity at Haddam, Middlesex County, Conn., but none is known to have been shipped.

The following table shows the production of lithium minerals in the United States for 1918 to 1928.

Lithium minerals produced in the United States, 1918 - 1928[1]

Year	Short tons	Value
1918	5,894	$111,600
1919	6,287	115,000
1920	11,696	173,002
1921	1,833	33,508
1922	2,192	41,300
1923	2,310	38,800
1924	2,996	62,391
1925	3,140	58,500
1926	3,700	53,400
1927	4,173	59,656
1928	4,600	94,750

1/ Mineral Resources of the United States, Part I. Published by U. S. Geol. Survey, 1918-1923. Published by U. S. Bureau of Mines, 1924-1928.

IMPORTS AND EXPORTS

No figures are available concerning the foreign trade in these metals or their compounds. Mineral waters, many of which contain lithium salts, are imported, and it is believed that from time to time small amounts of lithium metal are imported. Very small quantities of rubidium and caesium salts have been imported at intervals, but have not been shown separately in import statistics.

MARKETS AND PRICES

The market for caesium, rubidium, and lithium is extremely limited, and for lithium only is there any demand at present.

The principal market for lithium minerals is in the Eastern States. Practically all of the lepidolite mined in California is shipped in crude form to Wheeling, W. Va., and there pulverized for use in the glass trade. Most of the spodumene and amblygonite mined in South Dakota is shipped to Maywood, N. J., for conversion into lithium salts and chemicals.

The value of the lithium minerals depends, of course, largely upon their lithia content. In 1919 the following prices for crude ores prevailed;

Amblygonite, $50 to $60 per ton; spodumene, $20 to $25 per ton; and lepidolite, $14 to $20 per ton. Early in 1922 crude lepidolite was valued at about $18 per ton f.o.b. cars at mines in California. At the same time ground lepidolite sold for about $60 per ton (including bags) f.o.b. cars, Wheeling, W. Va. During 1928 amblygonite sold for $50 to $60 per ton, and spodumene for $20 to $30 per ton.

In purchasing amblygonite, buyers usually specify a minimum lithia (Li_2O) content of 8 per cent, as it has been found unprofitable to attempt to refine low-grade lithium minerals. Large quantities of lithium minerals are now unsalable due to their low lithia content as mined and prepared for shipment.

The following is a partial list of producers in lithium minerals;

Maywood Chemical Co., (Amblygonite and spodumene)
Maywood, N. J.

Consolidated Feldspar Co., (Amblygonite)
1005 Trenton Trust Bldg.,
Trenton, N. J.

Green and Collingwood, (Amblygonite)
Pringle, S. D.

National Industrial Chemical Corporation, (Lepidolite)
200 Madison Ave.,
New York, N. Y.

Pacific Minerals Co., (Ltd.), (Lepidolite)
Citizens Natl. Bank Bldg.,
Los Angeles, Calif.

Reinbold Metallurgical Co., (Amblygonite and spodumene)
103 S. 18th St.,
Omaha, Nebraska.

William Kay Wallace,
530 Fifth Ave.,
New York, N. Y.

The following is a partial list of possible purchasers and dealers in lithium minerals:

Philip S. Hoyt,
Las Tablas, N. M.

Minerals Conversion Co.,
Los Angeles, Calif.

R. T. Vanderbilt Co.,
50 East 42nd St.,
New York, N. Y.

Ward Leonard Electric Co.,
Mt. Vernon, N. Y.

A. D. Mackay,
26 Cortlandt St.,
New York, N. Y.

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Durand, M. J. F. The natural state of chemical elements and their cycles to the surface of the earth. Bull. Soc. Chim. de France, vol. 39-40, April, 1926, pp. 501-571. (In French from "Conference faite au College de France, Laboratoire de M. le Professeur, Ch. Moureu, le 30 Janvier, 1926.)

Hart, Edw., and Huselton, Henry B. Caesium alum and its properties. Jour. Am. Chem. Soc., vol. 36, 1914, pp. 2082-2084. The properties, chemistry, separation, metallurgy and uses of caesium, rubidium and lithium.

Hyatt, J. M. Secondary electron emission produced by positive caesium ions. Phys. Rev., vol. 29, 1927, p. 214; Chem. Abs., vol. 22, No. 21, pt. 1, Nov. 10, 1928, p. 4054.

Jakob, Johann. Rubidium and caesium-bearing mica. Schweiz, Mineralog. Petrog. Mitt., vol. 7, 1927, pp. 139-141; Chem. Abs., vol. 22, Jan. 10, 1928, p. 46. Complete analyses of the minerals are given.

Kastler, A. Treatment of pollucite (a caesium mineral) and preparation of caesium chloride. Bull. Soc. Chim. de France, vol. 41, 1927, pp. 428-434; Chem. Abs., vol. 21, July 20, 1927, p. 2232.

Kingdon, K. H., and Langmuir, Irving. Electron emission from caesium-covered filaments. Phys. Rev., vol. 23, 1924, pp. 112-113.

Kingdon, K. H., and Charlton, P. W. Caesium films in thermionic phenomena. Science, Dec. 14, 1928; Foot-Prints, vol. 2, No. 1, 1929, p. 20.

Koller, L. R., and Breeding, H. A. Characteristics of photoelectric tubes (caesium). Gen. Elec. Review, vol. 31, 1928, p. 476; Chem. Abs., vol. 22, No. 22, Nov. 20, 1928, p. 4387.

Langmuir, I., and Kingdon, K. H. Thermionic effects caused by vapors of alkali metals. Proc. Royal Soc., London, vol. 107, pp. 61-79. Discusses the thermionic effects of caesium under various conditions.

Larson, Alfred T. Caesium and aluminum increase activity of ammonia catalyst. Chem. and Met. Eng., vol. 31, Nov. 17, 1924, p. 769. Caesium and aluminum act to promote the catalytic of iron for ammonia synthesis. (U. S. patent 1,510,598 assigned to Arthur B. Lamb, trustee, Oct. 7, 1924.)

Loring, F. H., and Druce, J. G. F. Eka-Caesium. Chem. News, Nov. 6, 1925, p. 289. Quote spectrographic evidence of the discovery of an element of atomic number 87, which they have named eka-caesium.

Lunge, George. Potassium. Thorpe's Dict. Appd. Chem., vol. 5, 1924, p. 375. States that small quantities of rubidium, caesium, and ammonium and of bromide are always present in carnallite.

Machlett, Raymond R. Luminous tubes. Chem. Abs., vol. 22, No. 19, Oct. 10, 1928, p. 3556; United States patent 1,680,272, Aug. 7, 1928. The tubes contain a rare atmospheric gas, such as Ne, under reduced pressure and electrodes which may be mainly formed of graphite and which contain occluded alkali metal vapor - e.g., Cs.

Mathews, Irene Maud. The absorption spectrum of caesium. Proc. Roy. Soc. London, A 120, 1928, pp. 650-654; Chem. Abs., vol. 23, No. 1, Jan. 10, 1929, p. 34.

McCulloch, L. Vacuum tubes. Chem. Abs., vol. 22, No. 9, May 10, 1928, p. 1550. Alkali metals for use as "getters" and as photoelectric and thermionic films are introduced into vacuum tubes in the form of their trinitrides with or without trinitrides of alkali earth metals, and the trinitrides are decomposed by heat.

Meyer, H. C. Uncommon ores and metals. Eng. and Min. Jour., Jan. 21, 1928. On use of caesium in radio tubes.

Miesse, R. E. Production of metallic caesium. Chem. and Ind., London, vol. 48, No. 27, July 5, 1929, p. 526. A mixture of caesium chloride and a rare earth metal alloy is heated to 270° in an exhausted glass vessel until all traces of gas are removed and is then more strongly heated by radiation from an electric heater until reaction takes place with the production of caesium metal and rare earth chlorides.

Vernadsky, V. Acad. Imp. Sci., St. Petersburg; Trav. Musée Geol. Pierre le Grand, vol. 2, 1908, pp. 81-102. The author gives three-part analyses of beryl from which 3.10 per cent Cs_2O is obtained, which he calls vorobevite.

Zambonini, Ferrucio, and Coniglio, Luca. The presence of notable quantities of caesium in some products of present activity of Vesuvius. Atti. Acad. Lincei, (9) vol. 3, 1926, pp. 521-524.

Rubidium

Boer, de J. H., and Clausing, P., and Zecher, G. A simple method for the preparation of small amounts of metallic potassium, rubidium, and caesium. Ztschr. Anorg. Allgem. Chem., vol. 160, 1927, pp. 128-132; Chem. Abs., vol. 21, May 20, 1927, p. 1600.

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